EAST

Dissolved Oxygen and its Influence in the Self-Purification of Streams

Chemistry
B. S.

1901

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Dissolved Oxygen and Its Influence in the Self-Purification of Streams

. . . BY . . .

EDWARD MURRAY EAST

THESIS

FOR THE

Degree of Bachelor of Science in Chemistry

IN THE

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

E. M. East

ENTITLED Dissolved Oxygen and its Influence in the Self Purification of Streams

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF B. S. in Chemistry,

Arthur W. Palmer

HEAD OF DEPARTMENT OF Chemistry.

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PART ONE

HISTORICAL

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Dissolved Oxygen and its Influence in the Self-purification of Streams.

To reach a thorough understanding of the amount of the purification of running water; its causes and the influences of enviroment on its causes, is a task which has not yet been finished with sufficient accuracy and certainty to satisfy the minds of that part of the chemical world which is interested in water analysis. There are even now several chemists* of note who hesitate to admit that any natural purification other than a small oxidation and a large dilution, takes place. But the larger proportion of the authorities agree that there is a purification which takes place through natural causes, the amount of which has not been determined, and for which the causes are so varied that probably no definite ratio of purification to length of flow, exists.

The question is a broad one, each different phase of which, will take a long time to understand thoroughly and which will necessarily invlove much painstaking labor and experiment. The intention of this thesis is to compile, as far as library facilities will permit, the facts which are generally accepted in the present status of our knowledge concerning the self-purification of water. And then to take up that part of the work, which is in some way dependant on or show relation to the contents of dissolved oxygen. Even this small portion of the subject seems in

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*Wm. R. Nichols. Water P. 62.

itself to greatly enlarge when more than a passing thought is given it, and owing to the small amount of time available for the investigation, it is to be regretted that it can not be done more thoroughly.

It is an undisputed fact that the influence of water on the processes of plant and animal life is to be placed at least second in the triumvirate of influencing elements, air, water and soil: and some physicians as well as most scientists contend that morbific influences are more often conveyed through the instrumentality of water than by the atmosphere. A knowledge of the chemical and physical properties of pure and natural water in its three forms,- solid, liquid and gaseous, is an all important thing for the health officer; especially true of its solvent power on gases and saline bodies. Great strides have been made the last ten years in this direction, especially since 1881 when bacteriology first became a science; and as"this may be said to be still in its infancy, it is to be hoped and expected that much good will come from its continued study".*

To the chemist water is known as a compound of oxygen and hydrogen in the proportion of eight parts by weight of oxygen to one part by weight of hydrogen. At 760 mm. pressure and a temperature of 0.°C. it becomes solid, at 100° it becomes a gas or vapor. During its passage from the liquid to the solid state, water expands about one eleventh of its volume, so that ice at its melting point has the specific gravity of .9168 as compared with water at the same temperature. This fact and the one that at 4°C., water reaches its greatest density is of itself to greatly enlarge once more than a passing thought is given it, and owing to the small amount of time available for the investigation, it is to be regretted that it has not been done more thoroughly.

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*T. J. Burril, Ph. D.

It is an undisputed fact that the influence of water on the prevalence of plant and animal life is to be placed at least second in the trio-triad of influencing elements, air, water and soil; and some physicians as well as most scientists contend that morbific influences are more often conveyed through the instrumentality of water than by the atmosphere. A knowledge of the chemical and physical properties of pure and natural water in its three forms,- solid, liquid and gaseous, is an important thing for the health officer; especially true of its solvent power on gases and solids bodies. Great strides have been made the last ten years in this direction, especially since 1880 when bacteriology first became a science; and as this may be said to be still in its infancy, it is to be hoped and expected that much good will come from its continued study.*

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incomparable importance to the sanitarian. The freezing of masses of natural water at their surface, and the maintenance of the adjacent underlying strata at a temperature of 4°C. serve to permit the maintenance of the processes of animal life, and the spores or seeds of vegetable life in the aquatic organisms found in our ponds, lakes and rivers. Another fact with no connection to this, also due to the irresistable expansive force exerted by water during its solidification is the disintegrating action of water upon rocks and soils.

Water is the universal solvent. It dissolves or retains all the known gases; the degree of solubility depending on several conditions, as temperature, pressure, etc., besides the nature of the solute itself. It also dissolves and takes up to some extent, all known solid bodies, with the possible exception of the diamond and some of the noble metals. Even the most refractory minerals commonly termed insoluble, gradually yield to its solvent action, an action generally aided by the gases and salts already dissolved. It is thus that the streams and rivers are the conduits by which parts of the crust of the earth, partly dissolved, and partly held in mechanical suspension, are carried seawards and there deposited in the form of mud and sand, eventually to become new rocks; or retained in solution. Absolutely pure water, in the chemical sense of the word, is never found in nature, and is only obtained with great difficulty by repeated distillation. In the following pages, water will be spoken of, not in its chemically pure, but in its natural state; and in speaking of a pure water, purity is considered in a sanitary sense, meaning a water practically free from all

noxious gases, from injurious organic matters, and from injurious saline constituents; containing no excess of ordinary mineral ingredients, and no pathological micro-organisms : containing however , ordinary harmless and perhaps helpful saline ingredients in moderate quantities, as well as oxygne, nitrogen and carbon dioxide.

In their sixth report the Rivers Pollution Commision of Great Britain(1868), concluded from their researches that natural waters may be divided into seven classes in order of their fitness for domestic use:-

Wholesome.	1. Spring water.
	2. Deep well water.
	3. Upland surface water.
Suspicious.	4. Stored rain water.
	5. Surface water from cultivated land.
Dangerous.	6. River water to which sewage gains access.
	7. Shallow well water.*

This is a classification by source alone, and holds true if no unusual influences affect the waters. There can not be given any strict chemical composition for pure waters, the normal percentage of each constituent varying with each of these sources; with the location of the supply and with the time of year and climatic conditions. There has been tentatively suggested a standard table of maximum impurities for this state (Chem. Survey of Water Supplies of Ill. Preliminary Report. A. W. Palmer. 1897.)

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*Not unqualified.

Total solids-------------------500 parts per million.
Oxygne consumed--------------- 2 " " "
Chlorine---------------------------- 15 " " "
N.Nas free NH_3---------------- .02 " " "
N. as alb. NH_3---------------- .05 " " "
N as Nitrites---------------- .001" " "
N. as nitrates-----------------15. " " "

But each of these constituents may vary considerably with different conditions.

However, even if we accept the above classification as the proper one, it is only too evident that all cities can not have their choice of water supplies, and that there devolves on the city board of health a grave problem, which has only within the last decade had more than passing attention paid to it. And even now we have material evidences (W. P. Mason. Jnl. Frank. Inst. 143:337.) that it is not over studied; the public boards seemingly having greater responsibilities than knowledge of sanitary principles.

Everybody seems to be talking or writing about water, but the public is very far from being well posted upon the subject; and one encounters all sorts of odd views, which are remarkable not only for their character, but for the tenacity with which they are held. Ocular evidence of purity is quite sufficient for most people. The bright and limpid water from a well that drains a graveyard is counted a blessing by those who would shudder at the thought of a cholera ship touching at one of our most distant ports.

It can not be said that all water should be kept unpolluted, desirable as it is, for it is manifestly impracticalbe;

indeed a land should be looked upon as watered by its smaller lakes, springs, brooks and streams, and sewerad by its great, especially its navigqble rivers. But its water sources should be protected by law with exceeding care and no river or stream should be added to the list of drains, except after proper consideration by the state Board of Health, followed by legislative permission.

The relation of water to human health must be considered chiefly in the light of the changes which go on in the substances held suspended, or dissolved in it, and the effect of these changes on the wholesomeness of the water. (Air, Water and Food). Richards & Woodman. P. 52.) The suspended matters may be inert; as clay, sand and other inorganic matters; dead vegetable, as fragemnts of plants; living vegetable, as plants floating on the surface, diatoms, desmids, algae, and so forth; dead or living animal as infusoria, small crustaceans, etc. In another class may be placed, perhaps, all waste products of human activities, dejecta, factory wastes, garbage, etc., whereever these occur, there are found the lower orders of vegetable organisms, fungi, moles, bacteria, ready to do the necessary work of decomposition preparatory to solution. The mere presence of these forms of living matter does not of itself mean danger to those using the water but among these may be found pathogenic organisms which are at present, thought more likely to cause disease. Such microbes do not find in water a congenial habitat, but nevertheless thay do grow, and the danger from them is at all times a very real one. The presence or absence of these microscopic disease bearers, is something which the chemist cannot definitely decide

upon; he can only indicate that there is probable pollution of the water, and therefore danger.

No one in the present day (Hygiene. Stevenson and Murphy. p. 266) doubts that epidemics may be spread by means of drinking water, and the theories of physiologists that this is brought about by specific living germs or spores, have withing the last few years been confirmed by the actual discovery of the bacteria which are the active agents in propagating certain forms of disease. But whether the germs of disease present in drinking water are the actual direct agents in communicating disease, or whether the chemical products of the active changes invloved in the life history of these germs are the intermediate factors, is not yet altogether determined. There is evidence, however, tending to show that in some cases it is the living germ that causes the disease, and in others the bacteria may produce specifically toxic compounds. (Dr. S. Martin. 19th Re. Med. Officers Loc. Gov. Board. p. 235).

Diarrhoea and disentery are without doubt more often caused by impure water than in any other manner. There is some controversy, however, as to the spread of cholera by the agency of water, the evidence from all American and English investigations, points to the affirmative, but various eminent German authorities come to a different conslusion. (Zeit. f. Biol. Bd. 1; p. 353.) There has so much more been done, however, in England in this line of work that it is more probable that the theory of the English is the correct one. In typhoid fever, which annually kills in England, two people out of every ten thousand, bacteriology leaves no room for doubt concerning its cause.

The direct connection between the spread of typhoid fever and water supply has been for a long time one of the best established conclusions of modern medicine: and when the typhoid bacillus was discovered and the effects of its action proven by inoculation, it came as a mere support to the definite conclusions arrived at by statistical and individual inquiries into the cause of disease.

It is then to guard against these menaces to public health, that forms the great problem for the municipal engineer of today; and before speaking of the natural purification of water, it might be well to mention the artificial methods which are in use today. They may be divided into four different kinds, aeration, chemical precipitation, subsidence and filtration. The last two are by far the most important at present, although aeration and chemical precipitation are generally an adjunct to filtration.

In clarification by subsidence, the water is simply collected in large reservoirs for a variable period, depending on the size and kind of the dirt particles to be gotten rid of. In a great many places this method is practiced before the water is put through a filter. In a sedimentation such as this, the larger particles, in settling, carry with them many impurities that would otherwise be light enough to remain suspended in the water; and even matters in solution are carried down to a greater or less extent. At St.Petersburg, the waters of the Neva are clarified and rendered purer by a special process of aeration; the water being caused to fall in successive cascades, each a couple of feet high, upon wire gauze. The gauze soon becomes

covered with a black scum, and both an aeration and a bacterial action takes place, although the water before treatment is apparently clear.

After a treatment in subsidence reservoirs, the water is usually filtered through sand and gravel. The sand acts in part as a mechanical strainer, and in part as a condenser of oxygen and agent of oxidation; all finely divided particles having this property of condensing oxygen on their surface. Inthis state oxygen is much more active in bringing about oxidation.

As ordinarily constructed, a filter bed may be regarded as a U shaped tube with a short and a long limb; the longer limb, some ten feet in length, being represented by the bed of filtering material plus the superposed unfiltered water. The filtered water collects in the shorter limb. The water is forced downward through the filtering material by a pressure of water represented by the difference in level of the water in the two limbs of the apparatus.

The filtering medium may consist of a stratum of fine clean sand, two feet in depth, followed by eighteen inches of gravel of different sizes, the coarsest at the bottom. Below this there is a layer of from two to three feet of broken stone, the smallest at the top. The topmost layer of the sand is where the principal filtrations take place. The water usually stands at a depth of from four to six feet on top of these filter beds. The water passes through at a rate of about three gallons per square foot of surface per hour. The filters soon become clogged and have to be cleaned, thus the filters are worked intermittently, some of them always undergoing renovation, while others are working.

Filtration through sand alone, undoubtedly makes a more complete purification than is at first suspected. (Allen Hazen., Eng. Mag. v. 15; page 254.) Certain organisms attach themselves to the sand grains and remain fixed while the water flows past .

them, and they take from it as it passes the organic matters which forms their food supply, and which constitutes an objectionable matter in the water. This forms a"schleimdecke", or slime coat which is the real filtering material. As a result of this assimilation, the organic matter is converted into CO_2 and HNO_3, the latter combining with the alkaline earths always present in the water, form nitrates. It has been proven by experience that properly constructed filters of this kind, actually remove and destroy from 95 to 99 per cent. of the organic matters present in the sewage passing them, and at the same time remove the bacteria even more completely. Large numbers of bacteria find themselves incapable of existing in the presence of the many changes which are taking place in the filter, and thus lose their lives: others are removed by the straining.

At the Lawrence experiment station of the Mass. state board of health, filters are now in use, which have been constantly receiving sewage for ten years, yielding effluents rarely containing more than two per cent. of the organic matters, and sometimes not more than one in a million of the bacteria.

It has been said of water "that innocence is better than repentance", but honest and through going repentance is not to be despised. It is not despised by nature itself. And where the only sufficient sources of water within reach of a large city are polluted, we are justified in an attempt to correct the evil. But owing to the cost and inconvenience of artificial purification for city water supply, it is important to know just how them, and they take from it as it passes the organic matters which forms their food supply, and which constitutes an objectionable matter in the water. This forms a"sable cloth", or slime coat which is the real filtering material. As a result of this oxidation, the organic matter is converted into CO_2 and HNO_3, the latter combining with the alkaline earths always present in the water, form nitrates. It has been proven by experience that properly constructed filters of this kind, actually remove and destroy from 98 to 99 per cent. of the organic matters present in the sewage passing them, and at the same time remove the bacteria even more completely. Large numbers of bacteria find themselves incapable of existing in the presence of the many changes which are taking place in the filter, and thus lose their lives; others are removed by the straining.

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It has been said of water "that innocence is better than repentance", but honest and thorough going repentance is not to be despised. It is not despised by nature itself. And where the only sufficient sources of water within reach of a large city are polluted, we are justified in an attempt to correct the evil. But owing to the cost and inconvenience of artificial purification for city water supply, it is important to know just how much of this correction can be left to nature, herself.

About the year 1867 a statement was made by Dr.Letheby and others in England, that, if sewage is diluted to at least twenty times its volume, it will not only be made inoffensive, but the polluting matter or material, will be thoroughly destroyed after flowing "a dozen miles or so".

Dr. Frankland and the rivers pollution commision of Great Britain in 1878 maintained that no river in England was long enough to allow of a complete disappearance of sewage matter discharged into it.

Dr.Fleck (Ueber Flussverunreinigung. Jahresbericht der Kgl. chem. Centralstelle., Dresden, 1884) after an extensive inquiry into the subject in Germany, expresses his opinion that water is to be considered objectionable if in 1,000,000 parts there are contained 10 parts organic matter or 0.1 parts NH_3, and thinking this purification not possible.

But this position has been successfully contested by Odling, Tidy, and others. And Dr. Frankland has apparently, from his later writings, seen his way clear to modify his previous views as to the oxidizing powers of dissolved oxygen.

It is probable that the salts of iron (Hygiene. Stevenson and Murphy. v. 1: p. 264) always present in natural waters in very minute quantities act in some measure as carriers of oxygen. Putresent sewage reduces these salts to the lower stage of oxidation of ferrous salts, e.g. ferrous sulphide; and they, under the influence of dissolved oxygen, become converted into the ferric or more highly oxygenated salts, which again give up their oxygen to organic matter, and are again reduced to the state of ferrous salts.

Some think that iodine compounds, (Sonstadt (Chem. News V. 25 p. 196, 231, 241) finds 1 pt. $Ca(10_3)_2$ in 250,000 pt. sea water.) also rarely absent from terrestrial waters, act as carriers of oxygen, by their alternate oxidation into iodates, and reduction to the state of iodides.

Ordinary free oxygen , and still less atmospheric air , oxidize putrescible organic matters when in dilute solutions, only slowly in laboratory experiments such as Dr. Frankland's or Frederick Emich's experiments.

These experiments were of about the same nature. Dr. Emich got the following results by shaking with air 150 times per minute for 6 hours per day.

Contents of dissolved O at beginning ------------11.6 pts. per M.
Contents of dissolved O after 3 days ------------ 9.7 " " "
Contents of dissolved O after 6 days ------------ 8.0 " " "
Contents of dissolved O after 10 days ------------ 7.4 " " "
Contents of dissolved O after 14 days ------------ 6.6 " " "

This shows no marked oxidation.

Under natural conditions the effect is apparently different; where water is exposed to an enormous and practically unlimited supply of air; and it is probable that atmospheric ~~and~~ ozone and peroxide of hydrogen may have much to do with the effective oxidation of the nitrogenous organic matter present in the polluted waters of rivers. These agents have practically nothing to do with the oxidation of organic matter in the solis and water in the subsoil. Here a different agency comes into play. Nitrification depends upon an organism always of the soil, and does not extend, as a general rule, much below 18 in. below the surface. It may be expected that water from shallow wells , then, at a greater than this would be likely to contain

impurities of a disease producing character. But such is found to be the case only when the water is protected by an impervious layer of material such as clay. Moreover wells sunk to no greater depths in a gravelly soil frequently yield an organically polluted water. This difference from what might be expected, may be reconciled on the supposition that a well receives polluted water, or liquids, rapidly through the superficial and nitrifying layer of surface soil, so that the organic matters pass through the large pores and fissures in the soil, and thus escape the agency of those organisms which would otherwise convert the nitrogenous organic matter into harmless nitrates.

The enormous extent of the purification of streams effected by aquatic animal and vegetable life has been to little appreciated. (Rivers Pollution Commision. Sixth Report.) Where fresh sewage flows from a sewer into a stream, the mouth of the sewer becomes the feeding place of numerous small coarse feeding fishes, which greedily devour and convert into food for the larger fishes the scraps of muscular tissue and other debris which would otherwise decompose and pollute the water. Minute particles of solid organic matter may, and probable do serve as the food of minuter forms of animal life, and thus indirectly serve as food for fish. The mud banks of the Thames estuary are the habitat of the finest flat fish, eels and molluscs which serve the London market. But exceedingly putrid, sewage polluted streams, are shunned by aquatic animals, and ti is well known that stinking streams do not readily undergo self-purification. Nor must the beneficent effect of growing plants be ignored. Such plants, even those of a low type are capable, under the influence of sunlight, of effecting vast changes in the character of a water, by changing

the polluting nitrogenous matter into their own vegetable tissue in their growth. The cleaning out of tanks and ponds, in order to free them from weeds, has been known to render the water of such reservoirs more impure, by depriving them of a most active agent of purification.

Much waste material thrown into rivers is made up wholly or in part of substances insoluble in water. A portion, and a very considerable portion, of such matters even in a running stream is deposited upon the bottom, or stranded upon the banks.. This deposition can often be seen very plainly in the immediate neighborhood of points of discharge. It is not, however, suspended matters only that are removed by deposition. In the first place many substances which seem to be perfectly dissolved, are dragged out of solution and carried down by almost any finely divided substance. This is especially true of organic coloring matters and of the nitrogenous matter which gives rise to the "albuminoid ammonia" revealed by analysis: it is also true, but to a more limited degree, of some of the mineral salts. In the second place chemical changes take place in the stream, especially where refuse liquids from different sources meet and mix, which result in the formation of new and insoluble substances, and these when formed, settle out, dragging other substances with them,as just indicated.

The disappearance of organic refuse is, no doubt, to a certain extent, due to chemical changes, by which the organic matter is oxidized and converted into simpler compounds. Under favorable circumstances the destruction may be complete; the nitrogen appearing in ammoniacal compounds and nitrates, or escaping in the

free state, and the carbon appearing as carbonic acid. The greatest amount of this action is probably brought about by the smaller animal and vegetable inhabitants of the water, especially bacteria; indeed it is now thought that these microscopic organisms have more to do with the improvement of waters than all other causes put together. The action of the bacteria may be divided into two classes, that of the aerobic bacteria, which develope in greater numbers, and thus work more actively in air and light; and the anaerobic division, which develope under the conditions of, darkness, ill-ventilation and moderate heat, as shown in the working of the septic tanks which have lately come into use. The action of these two divisions has not yet been completely differentiated, but the action of the entire division of saprophytic bacteria, is looked upon as a benificial one. In the septic tank, for instance, this biological growth and activity produces a chemical decomposition of the retained organic matter of the sewage, a reduction of its compounds into parts, a large portion passing off in the form of gases (Co_2, N_2; CH_4, C_2H_6.) a part as inorganic matter with the effluent, and a part as silt-like sludge or ash which is deposited in the tank. (A. N. Talbot. Eng. News. 1897.)

Through the functional activities of the saprophytes, the highly complicated tissues of dead animals and vegetables are resolved into simpler compounds, carbonic acid, water and ammonia, in which form they may be taken up by the more highly organized members of the vegetable kingdom. It is through this ultimate production of carbonic acid, ammonia, and water by bacteria, as end products in the processes of decomposition and ferfree this, and the carbon appearing as carbonic acid. The greatest amount of this action is probably brought about by the smaller animal and vegetable inhabitants of the water, especially bacteria; indeed it is now thought that these microscopic organisms have more to do with the improvement of waters than all other causes put together. The action of the bacteria may be divided into two classes, that of the aerobic bacteria, which develope in greater numbers, and thus work more actively in air and light; and the anaerobic division, which develops under the conditions of, darkness, ill-ventilation and moderate heat, as shown in the working of the septic tanks which have lately come into use. The action of these two divisions has not yet been completely differentiated, but the action of the entire division of saprophytic bacteria, is looked upon as a beneficial one. In the septic tank, for instance, this biological growth and activity produces a chemical decomposition of the retained organic matter of the sewage, a reduction of its compounds into parts, a large portion passing off in the form of gases (CO$_2$, H$_2$; NH$_4$, H$_2$S) a part as inorganic matter with the effluent, and a part as silt-like sludge or muck which is deposited in the tank. (A. N. Talbot. Eng. News. 1897.)

Through the functional activities of the saprophytes, the highly complicated tissues of dead animals and vegetables are resolved into simpler compounds, carbonic acid, water and ammonia, in which form they may be taken up by the more highly organized members of the vegetable kingdom. It is through this ultimate production of carbonic acid ammonia and water by bacteria, as end products in the processes of decomposition and rementation of dead animal and vegtable tissues, that the demands of growing vegetation for these compounds are supplied.

In this way a double purification is accomplished; as the plants in their turn work a part in the improvement of the water.

The purification of sewage, is,therefore, a process of destruction of this organic matter by means of bacteria, and, finally of the bacteria themselves for inanition. It necessitates, their cultivation, and a provision of the most suitable conditions for their life and propagation, until the organic matter shall be converted and the conditions of their existance shall cease . According to Pasteur, the aerobies produce the oxidation into nitrates; while the anaerobies produce putrefaction. The aerobic process, when applied to organic matter in suspension is slower than the anerobic process. It takes a long time for solid particles of organic matter to dissapear as such, when the conversion depends on the oxygen contained in the water. It takes a short time , when it is brought about by anerobic bacteria, which produce conditions causing a liquefaction of the organic matter. The reverse seems to be true of organic matter in solution, because the aerobic bacteria, or conditions which favor a thorough aeration of liquid sewage, will remove a greater amount of organic matter from the water in the same time than if it is left to the action of anaerobies.

It may be seen by a study of these bacteriological actions that both kinds of bacteria need oxygen for their development,- for they both give off CO_2, * the difference being that only aerobies can take their oxygen directly from the air.

But, the aerobies are the principal active agents in all running streams, therefore they must get the oxygen which they

* Abbott. Principles of Bacteriology. P. 40.

use up from the air which is dissolved in the water. The dissolved O should then, furnish some criterion of the purity of the water, and it is upon this that the experimental part of this thesis has been done.

PART TWO

EXPERIMENTAL

The methods used in the investigation are those of Levy and Winkler. The original method by A. Levy may be found in Frémy's Enclyklopedia Vol. 91 p. 17. This give no special sized pipette, and a different amount of reagents from the method used. The method is described as follows in Tiemann and Gaertner p. 304. This method depends upon the fact that oxygen will readily convert ferrous hydroxide into ferric hydroxide. The only special apparatus needed, is a Levy pipette, which is a pipette with a stopcock at each end, made to hold exactly 107 c.c. At the upper end a small cylindrical funnel is attached while the lower end is drawn out into a small tube about 5 inches in length.

The reagents necessary for the determination are a solution of ammonium ferrous sulphate containing 40 g. of the crystallized salt to the litre: a 10% solution of KOH: a 50% solution of such a $K_2Mn_2O_8$ solution of such a strength that each c.c. of the solution equals one part of oxygen per million, when using 100 c.c. of water.

The method of procedure is as follows. Fill the pipette with the water to be tested allowing no air to enter. Add 2c.c. of the caustic potash solution to the funnel. Open the lower cock, then carefully open the upper cock, allowing the KOH to enter. Close both cocks. The funnel is then rinsed several times with distilled water. The lower tip of the pipette is kept standing in 2 or 3 c.c. of H_2SO_4, in order that if in the next step, adding exactly 5 c.c. of the ammonium ferrous hydroxide escape into the beaker, it will be changed into ferrous sulphate, which is not so easily affected by the air, and thus cause no error in the titration. After adding the ammonium ferrrous sulphate, the cocks are closed and the pipette shaken to mix the

reagents thoroughly in the water.

Then add 5 c.c. of the H_2SO_4 (1-1) to each funnel and open the upper cock only, the heavy H_2SO_4 displaces the lighter solution in the pipette and dissolves the ferrous hydioxide, and the ferric hydioxide formed by the oxidizing action of the oxygen dissolved in the water, forming ferrous and ferric sulphates. While this action is going on 107 c.c. of the water used, and 30 c.c. distilled water are placed in a beaker, 5 c.c. sulphuric acid, 2 c.c. of potassium hydioxide and 5 c.c. of ammonium ferrous sulphate solution added, and the ferrous sulphate titiated with standard potassium permanganate. The reagents should be added in the above order to prevent the formation of ferrous hydroxide by contact with air. When the solution is complete in the pipette, open the lower cock and allow the contents to flow into the beaker, rinse out the funnel with 30 c.c. distilled water, and titrate as quickly as possible with standard permanganate. The difference between the amount of permanganate used in the blank and in the determination, represents parts per million of oxygen.

THE WINKLER METHOD.

Berichte der Deutchen Chemischen Gesellschaft. 188 p.2843

This method depends on the facts that oxygen will readily convert manganous hydroxide into manganic hydroxide, and that manganic hydioxide in the presence of potassium iodide and hydrochloric acid will liberate iodine and be reduced to manganous chloride. The iodine set free is thus in a direct ratio to the oxygen contained in the water, and is estimated with n/1000 $Na_2S_2O_3$ and starch solution in the usual manner.

$Mn(OH)_2 + H_2O + O = Mn(OH)_3$

$Mn(OH)_3 + 3 HCL = MnCL_3 + 3 H_2O$

$MnCL_3 + HI = MnCL_2 + HCL + I$

The only special apparatus necessary is a bottle of known capacity that can be closed air tight.

After first washing the bottle of known volume several times with some of the water to be tested, fill to over-flowing and note temperature.

Add by means of a long narrow pipette, at the bottom of the bottle, 1 c.c. of 33% NaOH solution containing 100 g. KI per litre, and in the same way 1 c.c. of the $MnCL_2$ solution (of such a strength that volume for volume of the NaOH and $MnCL_2$ solutions will be equivalent). Insert the stopper and shake carefully. No air bubbles should be admitted in the addition of reagents and no air should remain on the closing of the bottle. Allow the precipitate to settle and add five c.c. of conc. HCL. (1.20), so that it will flow down the side of the bottle and bring strong acid in contact with precipitate. Replace the stopper with the proper precautions and shake until all the $Mn(OH_2)$ and $Mn(OH)_3$ are dissolved. If any oxygen was dissolved in the water we should now have free iodine present. Pour and wash the contents of the bottle into a large beaker (No. 5), add the starch indicator and titrate the iodine with n/100 $Na_2S_2O_3 + 5 H_2O$ solution.

The method is affected by the presence of nitrites and considerable organic material since nitrous acid liberates iodine from hydriodic acid, and organic matter takes up some iodine. In order to correct for the latter, the following

method is employed. Make a solution of $MnCL_3$ by adding 1 c.c. each of the $MnSO_4$ solution and of a 33% NaOH solution to 500 c.c. distilled water and stir well. Collect the precipitate on a small filter and wash; dissolve in conc. HCL. sp. gr. 1.20, dilute to about 500 c.c. and mix, to 100 c.c. of the water to be tested and to 100 c.c. of distilled water each, add 100 c.c. of the above $MnCL_3$ solution.

After 5 minutes add a crystal of KI to each and titrate the liberated iodine with n/100 $Na_2S_2O_3 + 5\ H_2O$ solution, using starch indicator. The difference between the two readings gives the correction to be added for each 100 c.c. of water to be tested as above for dissolved oxygen.

Since 1 c.c. of n/100 $Na_2S_2O_3 + 5\ H_2O$ solution is equivalent to 0.0000798 g. O. or 0.055825 c.c. of O. at 0°C. and 760 mm. pressure, then let V = contents of bottle; n the number of c.c. of sodium thiosulphate used in the first titration, N_2 the correction to be applied for the same volume of water and we have A the volume of dissolved oxygen (per litre of water) thus:- $A = \frac{0.055825(n + N_2) \times 1000}{V - 2}$ Multiplying A by 1.43 gives mg. dissolved O per litre of water.

The Levy method was first used in this investigation. The solutions were made up from the laboratory stock, with the exception of the oxalic acid, which was recrystallized in as small crystals as possible to make the exclusion of foreign matters as near perfect as possible, and then dried with ether, by placing the crystals on a Buchner funnel and washing through with ether.

To prepare a solution for standardizing the $KMnO_4$ solution:- 7875 grains of the pure crystallized oxalic acid was dissolved in distilled water containing 50 c.c. of strong sulphuric acid, and made up to one litre.

When 1 c.c. of this solution equals 1 c.c. of the $KMnO_4$ solution, then it is of such strength that 1 c.c. used in the titration of 100 c.c. of water equal to 1 part of oxygen dissolved per million.

The first series were from the Ill. and Miss. Rivers at Grafton, Ill. showing difference between the content of dissolved O at the top and bottom of the river. Then relying on the influence of bacteria in using up the dissolved oxygen, as was mentioned before, several series were run at different periods, from water collected at as near the same time and place as possible. The rapidity of dissapearance ought then to give an indication of the cultivating power of the water, in nourishing bacteria.

Note: (The places where the saturation is above 100 % are where the collector lost his thermometer and the temperature was estimated from that of the air, and may have been estimated too high. On the other hand (Migula Vol. II Manual of Bacteriology), oxygen may have been given off, by changes taking place in the animal and vegtable substances in the water, in such quantities as to make the water appear super-saturated.

DISSOLVED OXYGEN IN ILL. R. WATER

Collected at Grafton, Ill.

18 in. from Sur.

Date Collection.	Temp.	Time of Titration.	No cc for Blank.	Ave. Tit.	Pts.per Million	Per cent Sat.
11/19/1900	15° C.	11/20/1900	20.0	8.7	11.3	114.04
Ditto	15° C.	Ditto	20.0	8.7	11.3	114.04
11/26/1900	6° C.	11/27/1900	20.1	8.9	11.2	87.36
Ditto	6° C.	Ditto	20.5	9.2	11.3	88.15
12/3/1900	6° C.	12/4/1900	18.9	8.6	10.3	80.34
Ditto	6° C.	Ditto	18.9	8.6	10.3	80.34
12/11/1900	2° C.	12/12/1900	19.0	7.3	11.7	84.36
12/17/1900	1° C.	12/18.1900	18.9	5.6	13.3	93.20
11/12/1900	a=18° C.	11/13/1900	22.0	13.5	8.5	89.01
Ditto	a=18° C.	Ditto	21.8	13.6	8.2	85.87

DISSOLVED OXYGEN IN ILL. R. WATER

Collected at Grafton, Ill.

Two feet from Bottom.

Date Collection	Temp.	Time of Titration.	No.cc. for Blank.	Ave. Tit.	Pts.per Million	Per cent Satura.
11/19/1900 3 P. M.	15° C	12/20/1900 10.30 A.M.	20.0	8.9	11.1	109.47
Ditto	15° C	Ditto	20.0	9.1	10.9	107.49
11/26/1900 2.30 P.M.	6° C	11/27/1900 10.30 A.M.	20.7	8.7	12.0	93.60
Ditto	6° C	Ditto	20.6	9.6	11.0	85.80
11/3/1900 2 P.M.	6° C	12/4/1900 10.30 A.M.	19.1	9.3	9.8	76.53
Ditto	6° C	Ditto	19.2	9.4	9.8	76.53
12/10/1900 2.30P.M.	2° C.	12/10/1900 10.30 A.M.	19.0	6.6	12.4	89.40
12/17/1900 2.30 P.M.	1° C	12/18/1900 10.30 A.M.	18.6	6.0	12.6	88.30
11/12/1900	a=18° C	12/13/1900	21.0	13.5	7.5	78.52
11/12/1900	a=18° C	Ditto	21.1	13.5	7.6	79.58

DISSOLVED OXYGEN IN MISS. R. WATER.

Collected at Grafton, Ill. 18 in. from Surface.

Date Collection	Temp.	No.cc.for Blank.	Ave. Tit.	Pts. per Million.	Per cent. Saturation.
11/19/00	15° C	21.4	8.3	31.1	129.18
Ditto	15° C	20.5	7.8	12.7	125.26
11/26/00	6° C	20.2	8.0	12.2	95.16
Ditto	6° C	20.3	8.0	12.3	95.95
12/3/00	4° C	19.5	7.8	11.7	91.25
Ditto	4° C	19.0	7.6	11.4	88.92
12/10/00	3° C	19.1	4.8	14.3	105.94
12/17/00	1° C	18.8	5.8	13.0	91.10
11/22/00	a=18° C	21.1	10.3	10.8	113.09
Ditto	a = 18° C	21.3	9.8	11.5	120.44

DISSOLVED OXYGEN IN MISS. R. WATER.

Collected from Grafton, Ill. Two feet from Bottom.

Date Collection.	Temp.	Time of Titration	No.cc.for Blank.	Ave. Tit.	Pts.per Million.	Per cent Sat.
11/19/00	15° C	11/20/00	20.4	7.9	12.5	123.28
Ditto	15° C	Ditto	20.4	7.8	12.6	127.16
11/26/00	6° C	11/27/00	20.5	8.9	11.6	90.48
Ditto	6° C	Ditto	20.7	8.8	11.9	92.82
12/3/00	4° C	12/4/00	19.4	8.5	10.9	85.03
Ditto	4° C	Ditto	19.5	7.9	11.7	91.27
12/11/00	3° C	12/12/00	19.3	6.4	12.9	95.56
Ditto	3° C	Ditto	19.4	6.2	13.2	97.78
12/17/00	1° C	12/18/00	18.7	5.3	13.4	93.90
11/22/00	a=18° C	12/13/00	20.6	11.1	9.6	100.53
Ditto	a=18° C	Ditto	21.3	10.0	11.3	118.32

TABLE SHOWING THE DISSAPEARANCE OF DISSOLVED O. in Illinois River Water, Grafton, Illinois.

Standing in Closed bottles in the dark.

Pts. per million given.

Average titration only, given.

Two feet from bottom.	After 20 hrs.	After 50 hrs.
Collected 12/10/1900	12.4	12.0
18 in. below surface.		
Collected 12/10/1900	11.7	10.8

Two feet from bottom	29 hrs. after.	50 hrs. after.	75 hrs.after.
Collected 12/17/1900	12.6	11.5	11.0
18 in. below surface			
Collected 12/17/1900	13.1	12.2	11.2

TABLE SHOWING THE DISSAPEARANCE OF DISSOLVED O.
IN MISS. RIVER WATER.

Upon standing in closed bottles in the dark.

Pts. per Million given.

Two feet from bottom.	20 hrs. after Collection.		50 hrs. after Col.
Col. 12/10/1900	12.9	Aver. = 13.0	12.5
Ditto.	13.1		
18 in. from surface.			
Collected 12/10/1900	14.3		12.8

Two feet from bottom.	20 hrs. after.	50 hrs. after.	75 hrs. after.
Collected 12/19/1900	13.4	13.2	12.1
18 in. from surface.			
Collected 12/17/1900.	13.0	12.2	11.5

A series of samples of water showing the dissapearance of dissolved Oxygen in the Illinois R. water on standing. Two feet below Surface.

Collected Feb. 21, 1901. 2.30 P.M. Temp. air 78° F.

Titration, Time of	Pts. per Million.
After 20 hrs.	10.68
After 92 hours.	10.48
After 130 hours.	9.11
After 178 hours.	6.63
After 226 hours.	3.68
After 274 hours.	.49

Ditto series of samples from the Miss. R. Both series collected at Grafton, iLL.

Collected Feb. 21, 1901. 2.30 P. M.

Titration, Time of.	Pts. per Million.
After 20 hours.	10.67
After 92 hours.	10.52
After 130 hours.	10.48
After 178 hours.	9.94
After 226 hours.	9.10
After 274 hours.	8.06

Water from what is known as the boneyard was next tested by the same method. The boneyard is a small stream, a branch of Silver Creek which carries away a large portion of the surface water of Champaign and Urbana. Normally it contains about three inches of water. It usually goes dry in Summer, and sometimes overflows its banks after a heavy rain. It is a receptacle for a great deal of sewage and decaying organic materials. The stream is full of obstructions and in all probability within a hundred yards the water is all exposed to the action of the air. During low water the quantity of organic matter is but little less than in sewage itself.

The samples of water were collected just West of the University power plant, by means of an Empress syringe with a two ft. rubber tube extension on the delivery end. The Empress syringe is merely a tube, enlarged to a bulb in the middle and having a valve on each side. The valves are so arranged that when the bulb is compressed the lower one closes and the upper one opens, and vice versa. Eight compressions of the bulb fill the bottles used, but each were filled about three times.

The samples were run at intervals of 24 hours, to establish a ratio of dissapearance of the dissolved oxygen by bacterial action as in the former case. Nitrites and free ammonia were also determined. The free ammonia, merely by the nesslerization of the water itself and the nitrites by the usual method, relying on the red color which nitrites produce when added to a solution of napthylamine hydrochloride and sulphanilic acid.

Diminution of both free ammonia and nitrites was observed, but the ratio was not quite so regular as that of the dissolved oxygen.

This seems to indicate the predominance of nitrifying bacteria although the contents of nitrates were not determined.

Three series were run with the following results.

1st SERIES.

TABLE SHOWING DISSAPEARANCE OF DISSOLVED O.

in Silver Creek, Urbana, Ill.

Temp. 8°C.

Date.	Dissolved O.		Nitrites.	Free NH_3.
11/26/1900	11.4	11.7	.46	
2nd Sample	11.9			
After 24 hrs.	10.4	10.0	.44	
2nd Sample.	9.6			
After 48 hrs.	8.2	8.1	.40	
2nd Sample	8.0			
After 72 hrs.	6.8	6.4	.42	
2nd Sample	6.0			
After 96 hrs.	5.2		.32	

2nd. SERIES.

TABLE SHOWING DISSAPEARANCE OF DISSOLVED OXYGEN

in Silver Creek, Urbana, Ill.

Temperature of Collection 9° C.

Date.	Dissolved O. pts. per Million.		Nitrites. pts. per Million.	Free NH_3 pts. per Million.
12/5/1900	8.7	8.8	.32	.60
2nd. Sample	8.8		.32	.58
After 24 hrs.	8.0	8.0	.20	.60
2nd. Sample.	8.0		.20	.60
After 48 hrs.	6.8	6.9	.175	.54
2nd. Sample.	7.0		.175	.54
After 96 hrs.	5.6	5.9	.15	.40
2nd. Sample.	5.8			
After 144 hrs.	2.9	3.1	.15	.40
2nd Sample.	3.2			
After 168 hrs.	2.4	2.4	.12	.40
2nd. Sample.	2.3			

3rd. SERIES.

TABLE SHOWING DISSAPEARANCE OF DISSOLVED O. in Silver Creek Water, Urbana, Ill.

T. = 2° C.

Date.	Dissolved O.	Nitrites.	Free NH_3.
12/13/1900	8.7	.26	.62
2nd. Sample.	8.5		
After 96 hrs.	7.2	.18	.50
2nd. Sample.	7.0		
After 120 hrs.	6.1	.18	.48
2nd. Sample.	5.8		
After 144 hrs.	4.1	.15	.44
2nd Sample.	4.0		
After 168 hrs.	3.6	.15	.32
2nd. Sample.	3.4		

In doing the work of making the foregoing determinations several phenomena were noticed. The first was, that in making determinations of O. in waters containing large amounts of organic matter, that the duplicate should be run within thirty seconds of the first titration in order to get an accurate result.

If some time elapses between the two tritations there is a reduction of the ferric sulphate takes place. This gives a larger amount of ferrous sulphate than should be there, and makes a lower indication of dissolved oxygen, by taking a larger amount of $KMnO_4$ solution for the oxidation. This would seem to be due to the presence of nitrous acid, as is shown in the following table.

BONEYARD WATER CONTAINING HIGH NITRITES AND HIGH ORGANIC MATTER.

The first two results are from titrations run at as nearly the same time as possible, while the third was titrated after standing for ten minutes after adding the H_2SO_4.

Note: These samples were collected in 500 c.c. flasks.

Results in parts per Million.

(1)

1. = 8.8)
) 3. = 7.1
2. = 8.2)

(2)

1. = 9.1)
) 3. = 9.0
2. = 8.9)

(3)

1. = 8.6)
) 3. = 7.5
2. = 8.3)

(4)

1. = 9.2)
) 3. = 8.6
2. = 9.0

(5)

1. = 10.2)
) 3. = 9.1
2. = 9.8)

Same on tap water which is free from nitrites, though containing some organic matter.

(1)

1. = 10.2)
) 3. = 10.2
2. = 10.3)

(2)

1. = 10.4)
) 3. = 10.2
2. = 10.4)

2nd.

In running the determinations of dissolved O. by Levy's method upon N. free distilled water, the solution after adding the sulphuric acid, was found to keep a brown color with but slight fading even after an hour's standing. This color does not seem to interfere with the results obtained, but makes the end point of the titration difficult to see.

Ordinary natural water clears up as follows, the first figure given being the time taken for the water to clear up sufficiently for a good titration to be made, and the second, the time for a complete clearing up.

Surface well water. (501 Daniel St.)	4 min.	10 min.
Deep well water (John St.)	5 min.	13 min.
Tap water (Deeper strata than 2)	4-5 min.	13 min.

Effects of different solutions of various salts in N. free water, were tried with the following results.

2500 pts. per million NaCl.	6 min.	10 min.
1500 pts. per million NaCl.	6 min.	10 min.
500 pts. per million NaCl.	6 min.	13 min.
1000 pts. per million $MgSO_4$.	1 min.	5 min.
500 pts. per million $MgSO_4$.	5 min.	11 min.
800 pts. per million $CaSO_4$.	1 min.	4 min.
400 pts. per million $CaSO_4$.	3 min.	8 min.
100 pts. $CaSO_4$ 100 pts. $MgSO_4$ per million	4 min.	10 min.
100 pts. $MgSO_4$ 100 pts. NaCl per million	6 min.	13 min.
100 pts. $MgSO_4$ 100 pts. $CaSO_4$ 100 pts. NaCl	2 min.	8 min.

Continuation of the effects of salts in N. free water.

Bubbled CO_2 through for 10 min.	5 min.	12 min.
Saturated part above with $CaCO_3$	5 min.	10 min.
Saturated part of above with $MgCO_3$	3 1/2 min.	9 min.

The results of this series show that although all the salts normally contained in natural waters have some effect on dissolving or clearing away this brown color, that $CaSO_4$ and $MgSO_4$ have the most effect. They seem to have no effect on the accuracy of the titration and in some cases of waters that do not clear up readily a small amount of $MgSO_4$ might be added with impunity.

The third point investigated was the fact that in making determinations of dissolved oxygen under ordinary conditions, the titration must be made immediately in order to get accurate results; on account of the dissapearance of the dissolved oxygen upon standing. The rate of dissapearance varies with different waters, as can be seen in the foregoing tables.

As it is sometimes impracticable to make the determinations immediately and any means to keep the content of dissolved oxygen the same until the determinations could be made, would be acceptable. First the difference in dissapearance of dissolved oxygen in samples kept at different temperatures was tried. Ten samples of water were collected from the same place in the "boneyard", Oct. 29, 1900. Half were kept in a warm part of the laboratory at a temperature of about 25°, and half were kept in the coldest part of the basement at a temperature of about 10° C., and determined every 24 hours.

Results:-

Pts. per Million.

At time of Collection.	8.2	
	In Warm	In Cold.
After 24 hours.	6.9	7.5
After 48 hours.	5.6	7.3
After 72 hours.	4.5	7.0
After 96 hours.	4.4	6.2

This shows quite a marked difference due to the incubating effect of heat on the bacteria contained in the water.

The effect of sterilization was next tried upon water from a tap of the laboratory. The water was collected with great care for the first series. To the tap a tube was attached, reaching to the bottom of the receiving bottle. The water was allowed to run about 5 minutes and the samples then taken. The temperature was 12° C.

The second series was tap water collected in a large bottle and saturated with air from the blast, and then drawn off by syphon into bottles. In each series one half of the samples were corked air tight just as they were collected; to the other half 0.5 c.c. of a saturated solution of $HgCL_2$ was added. Results were as follows.

A series of samples of water from the Tap showing the difference in the ratio of dissapearance of the dissolved Oxygen in pure samples and in samples sterilized with Mercuric Chloride.

Temp. 18°.	Pts. per Million. Sterilized.	Pts. per Million. Not Sterilized.	
At time of Collection.			
After 24 hours.	5.71	5.72	2/18/01
After 48 hours.	5.61	2.49	2/19/01
After 72 hours.	5.61	1.03	
After 96 hours.	5.60	.65	
After 120 hours.	5.54	.42	

DUPLICATE SERIES. TAP WATER.

	Pts. per Million. Sterilized.	Pts. per Million. Not Sterilized.
At time of Collection.	9.7	9.7
After 24 hours.	9.68	7.64
After 48 hours.	9.68	5.91
After 72 hours.	9.62	3.42
After 96 hours.	9.62	2.12
After 120 hours.	9.58	1.03

The oxygen in the unsterilized bottles dissapear rather more rapidly than would be expected in such a pure water. But the unsterilized condition of the bottles and the organic material which might act as a nutrient medium for bacteria, might account for this.

It is well to know however that mercury forms several compounds with organic constituents such as might be contained in natural waters.

In order to determine whether these compounds have any specific effect on the dissolved oxygen of water, a series of samples was run after being sterilized by heat, thus leaving no chance for any chemical reactions outside of those among the constituents themselves to take place.

A two litre bottle was filled with sewage from a manhole, collected by letting down a bucket. This water was sterilized in the bottle for 1 hour and 30 minutes on 3 successive days. The bottle was fitted with a syphon passing through the cork and having a rubber pinch cock attached to the longer arm. Through the cork there also passed a $CaCl_2$ drying tube containing a cotton plug. After sterilization the water was saturated with air at 22° C.
The air was sterilized by passing through tubes containing a succession of six cotton plugs. The end of the glass tube after the last cotton plug was sterilized in the flame. After thorough saturation the water was used to fill five small bottles of the size ordinarily used for collecting samples of dissolved oxygen. These bottles had been sterilized under 10 pounds pressure for 30 minutes in an autoclave.
(Note: one c.c. of this water was plated upon gelatine in a sterile Petri dish and showed sterile aftdr 4 days).

These samples were determined every 24 hours with the following results.

Time.	Pts. per Million.
Immediately after saturation.	8.70
24 hours after saturation.	8.70
48 hours after saturation.	8.62
72 hours after saturation .	8.62
96 hours after saturation.	8.56

These results in comparison with those sterilized by $HgCl_2$, show no difference not covered by experimental error.

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During the time that these experiments were being made, two series of determinations were made in connection with the saturation of water with oxygen at a given temperature.

In the 1st series N free distilled water was used and the water saturated by shaking. Water was found to become saturated by about 5 minutes vigorous shaking, and did not easily give up its oxygen. The temperature was taken accurately and the determination of oxygen made immediately by Levy's method.

These results are slight lower than those used by analysis as a standard. Part of this may be due to experimental error, and part to the fact that the standards were determined at the sea level, while here theheight is over 600 ft. above the sea level, and the saturation point varies slightly with the pressure.

Results:	Parts per Million No. of determinations.				Standard for Temperature given.
Temp. C.	1	2	3	4	
-	-	-	-	-	---

Results to be placed in this form for comparison.

A determination of the saturation points of Oxygen dissolved by Levy's method.

Double distilled, Ammonia free water was used. Saturated with air by shaking at as near the titration temperature as possible.

Temperature.	Results in parts per Million.					
Degrees C.	1	2	3	4	5	6
10	11.25					
11.4	10.91					
13.2	10.51					
14.4	10.26	10.32				
16.0	19.93					
16.8	9.70					

Saturation Points ... Continued.

Temperature.	Results in parts per Million.					
Degrees C.	1.	2.	3.	4.	5.	6.
19.8	9.22	9.26	Recalculated with standardization made immediately after making results.			
20.7	9.03	9.03	9.06	9.07		

A comparison was now made of the Levy method with the Winklers method, using first N free distilled water, and then some pure surface well water and saturating as before. The $Na_2S_2O_3$ for the Winkler titration was standardized by $K_2Cr_2O_7$ which was neutralized and then melted.

The $KMnO_4$ for the Levy method was then standardized with oxalic acid. Then the KMnO4 was used to standardize the $Na_2S_2O_3$, thus getting an exact check on the two solutions. As a result .000197 g O from the $KMnO_4$ should equal the same from the $Na_2S_2O_3$:- .000199 was the actual results. Showing 1 % difference on amount determined which is within the experimental error.

A bottle containing 254.53 c.c. at 15° C. was always used. The calculations would then be as follows:

$$W + 0 \text{ per } L = \frac{.0000797(\overset{\text{Mo cc.}}{n/100}\ Na_2S_2O_3) \times 1000.}{254.53 - 2.0}$$

Then 7.49969 + Log. of No. c.c. N/100 $Na_2S_2O_3$ = log. of wt. of 0 in grains.

1st SERIES. N free water.

Temp. C.	No. cc N/100 $Na_2S_2O_3$	Pts. per Million.	Levy. Pts. per Mil	Standard table of pts of saturation.
16.8°	30.92	9.77	9.84	9.78
18.4°	29.84	9.43	9.56	9.45
20.3°	28.74	9.08	9.20	9.10
24.0	26.8	8.47	8.55	8.50
26.6°	25.6	8.09	8.14	8.10

2nd. SERIES.

Good surface well water containing no nitrites.

Temp. C.	No.ccN/100 $Na_2S_2O_3$	Pts per Million	Levy. Pts. per Million	Standard table of pts. of saturation.
17.2°	30.8	9.73	9.8	9.71
19.0°	29.7	9.39	9.42	9.32
19.2°	29.6	9.35	9.35	9.28
19.6°	29.32	9.26	9.35	9.24
20.0°	29.04	9.18	9.24	9.18
20.1°	28.81	9.10	9.20	9.13
20.2°	28.64	9.05	9.00	9.13
20.2°	28.44	8.99	9.00	9.13
22.5°	27.64	8.73	8.82	8.50
24.1	26.85	8.48	8.56	8.49

The final experiment of the investigation was to determine, if possible, the relation between the disappearance of dissolved oxygen in water, and the increase in the number of bacteria in the same sample.

A series of sewage samples were collected, in the usual manner. The dissolved oxygen in these samples was determined every twenty-four hours. At the same time one cc. of the water water was diluted to one hundred cc. with sterilized, distilled water. One cc. of this was then diluted to one hundred cc. in the same manner. One cc. of this dilution was then mixed with five cc. of agar cultivating medium and plated out, at 40°C. on a sterilized Petri dish. Two such plates were made each day: one plate being incubated at 37.5°C., and one kept at the temperature of the air. After a day or two of cultivation colonies of bacteria appeared on the media and were counted.

The bacteria were found to increase as the dissolved oxygen increased, up to the point where there was less than one part per million; from this point there was a sudden decrease owing to the fact that there was no oxygen for the support of the organisms.

This work was done in collaboration with Mr. H.T.Graber and Mr.E.L.Wait.

Table of results on next page.

Table showing the increase of bacteria with the decrease of oxygen dissolved.

Date Collection.	Temp. Collection.	Date Examination.	Pts Ox.	Per cent Saturation.	No. Colonies.
5/14/1901 11 A.M.	17°C.	5/14/1901 1 P.M.	3.73	37.52	2000000
"	"	5/15/1901 8 A.M.	3.7	37.22	3000000
"	"	5/16/1901 9 A.M.	1.67	16.8	2500000
"	"	5/17/1901 10 A.M.	1.33	14.38	3000000
"	"	5/18/1901 10 A.M.	0.98	9.96	4000000
"	"	Sunday.			
"	"	5/20/1901 10 A.M.	0.35	3.49	10000000
"	"	5/21/1901 10 A.M.	0.70		4000000
"	"	5/22/1901 10 A.M.	0.63		100000

Conclusion.

The results of this investigation have all coincided with the theory that dissolved Oxygen furnishes a criterion of the purity of a water by the relative quickness of its disappearance on standing. The larger the amount of organic matter contained in the water, the better cultivating medium is the water, and the faster will the bacteria develop at the expense of the dissolved oxygen.

Under the conditions of this investigation, (the water used for comparing the two methods was pure water containing very little organic matter and no nitrites) the two methods gave nearly the same results, the error being about one per cent of the amount determined, and is covered by experimental error. There seems to be, however, no regularity of difference between the two methods; sometimes one is the higher, and sometimes the other. This fact also would seem to show that the difference is due to experimental error. In manipulation, however, the Levy method is much the simpler; the solutions keep longer, the determinations may be made quicker, and the results are less affected by the conditions of the water.

The subject as a whole, however, is a very broad one, and will require a great deal of investigation, particularly on the bacteriological side.

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